Fifth Annual Conference on Carbon Capture & Sequestration

Steps Toward Deployment

Terrestrial Sequestration (1) Terrestrial Carbon

Advances in Calibrating Laser-Induced Breakdown Spectroscopy (LIBS) for Measuring Total Soil Carbon

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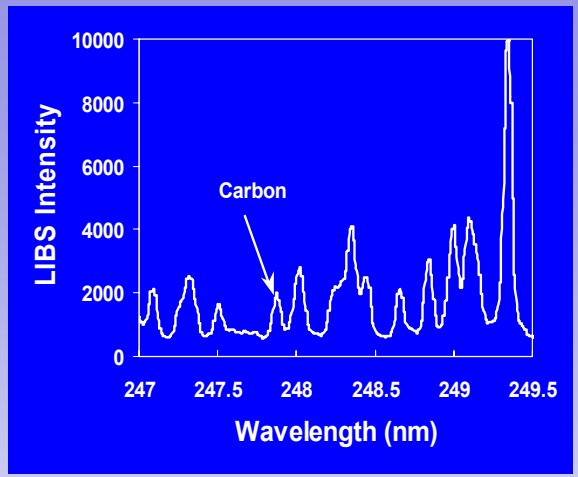
Laser-Induced Breakdown Spectroscopy

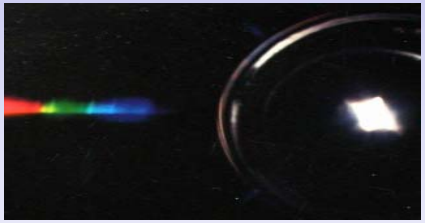
Laser Spark on Soil

- Nd:YAG Laser 532 or 1064 nm
- Usually pulsed at 10Hz
- ~ 1mm spot size

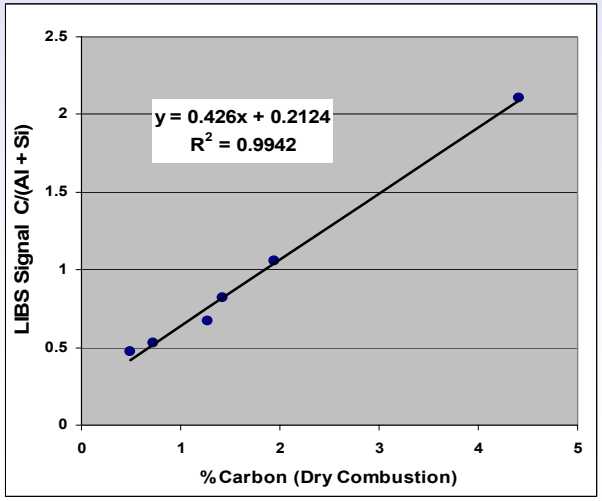


Emission Spectrum

Light from Plasma

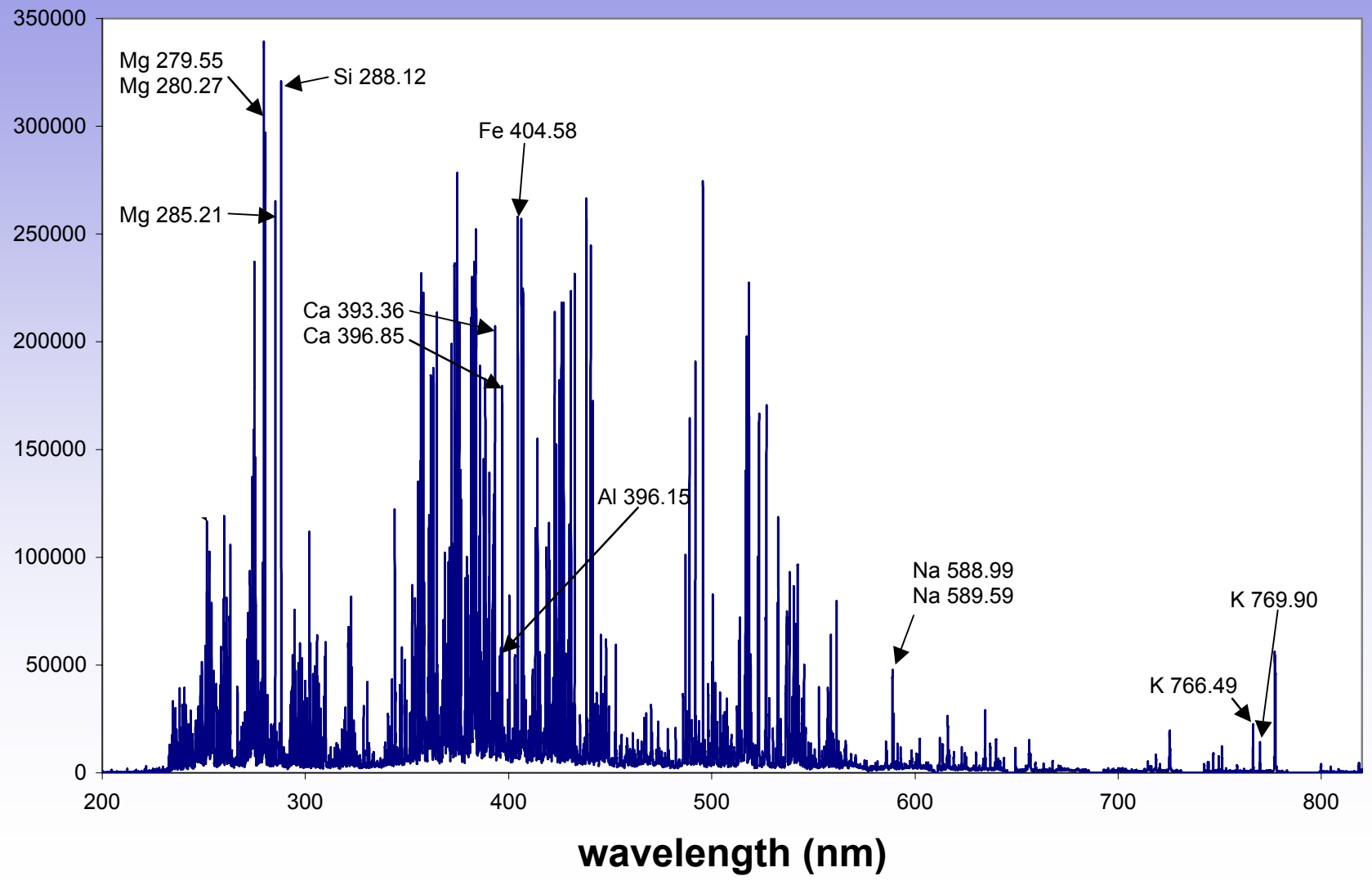


Calibration Curve



- **Interrogates the soil using a laser beam (~ 30 to 100 mJ)**
- **Provides information on elemental composition**

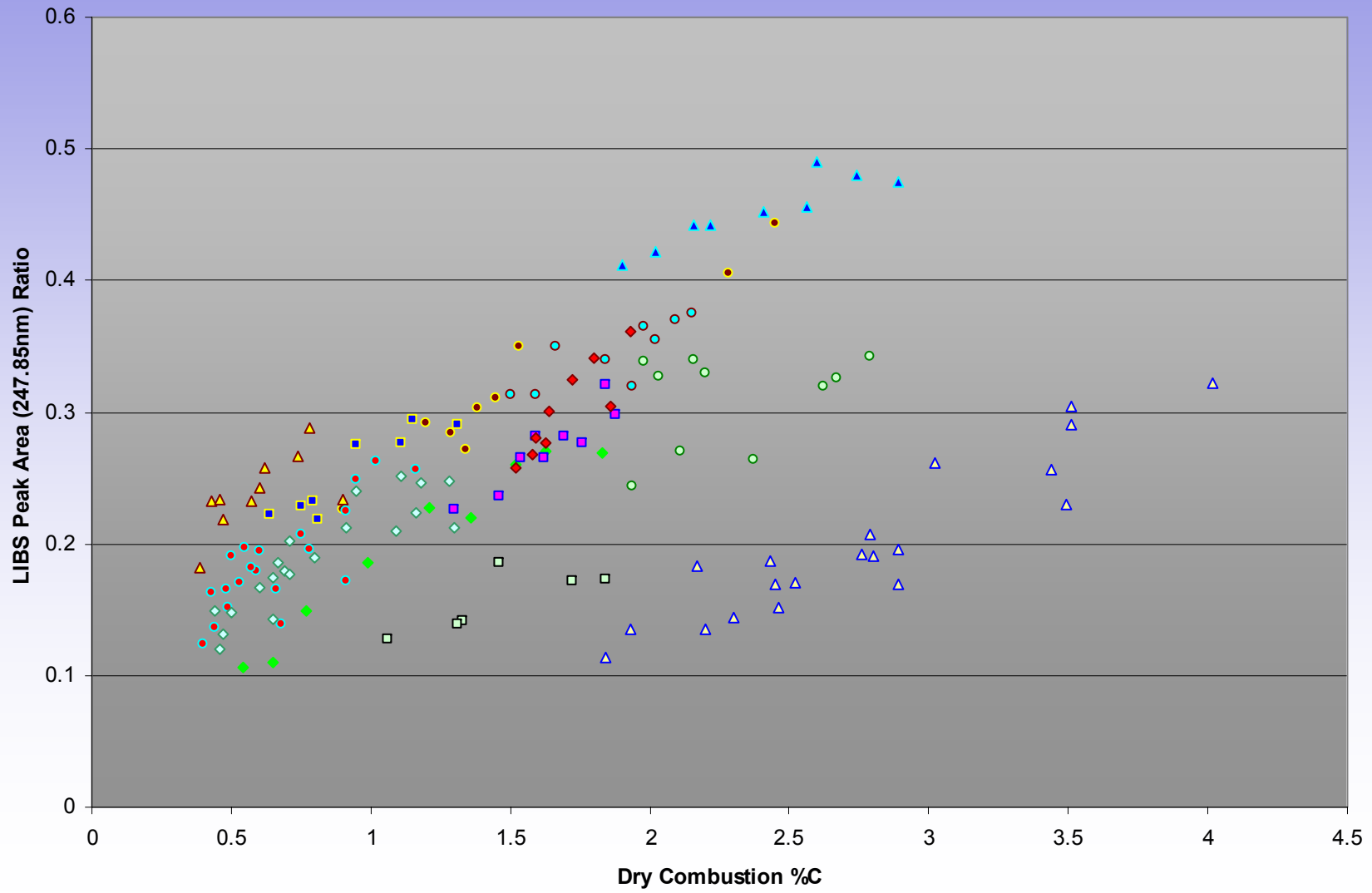
LIBS Spectrum: Provides Much Information



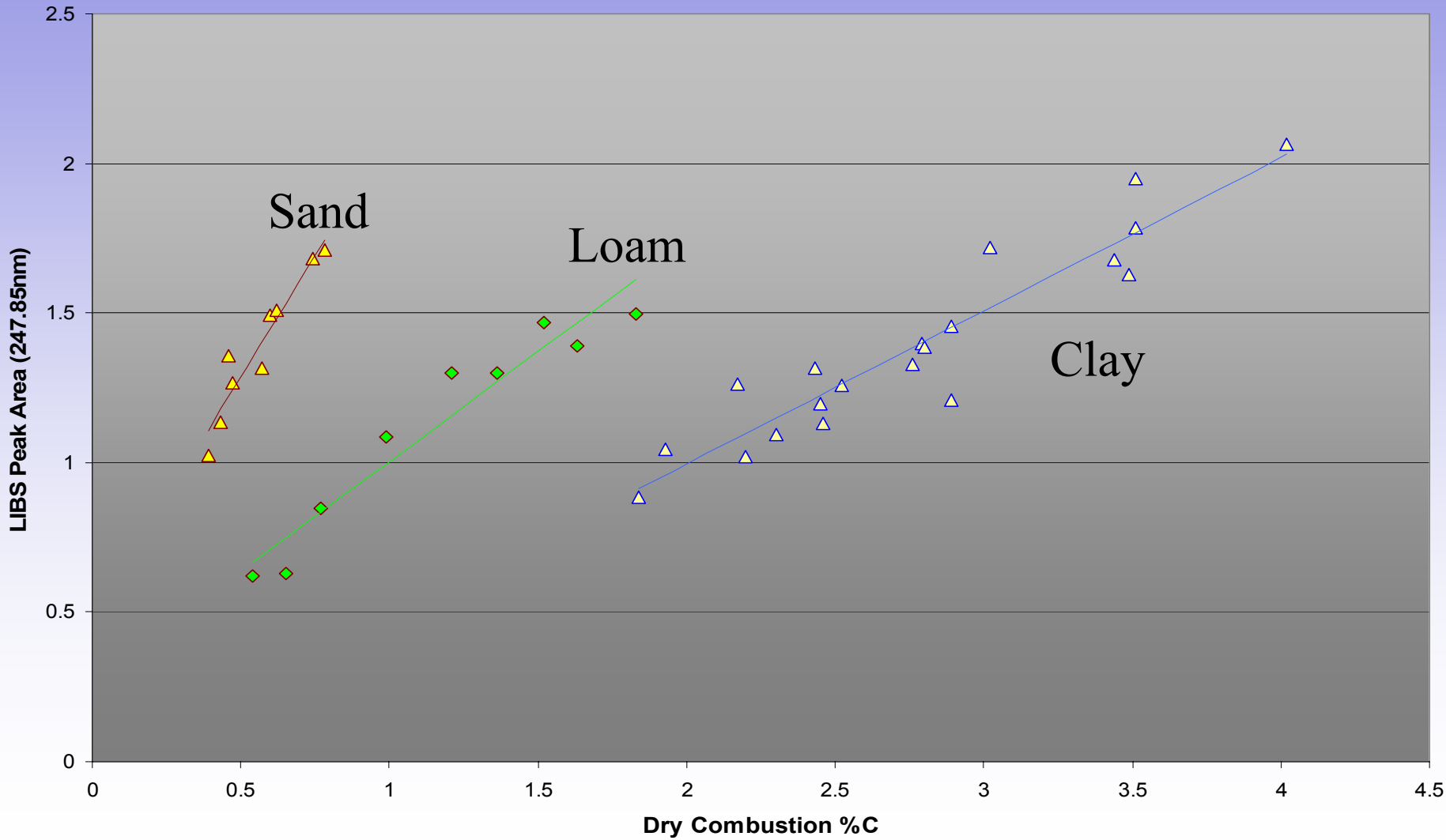
Sample Analysis at LANL

- Obtained ~200 soil samples from fields in North Dakota, Iowa, Michigan & Illinois
- Samples represented a variety of textures with combinations of sand, silt and clay
- Pressed samples into 30 mm disks for LIBS analysis to determine total soil carbon
- Performed dry combustion analysis on soils for comparison with LIBS signal

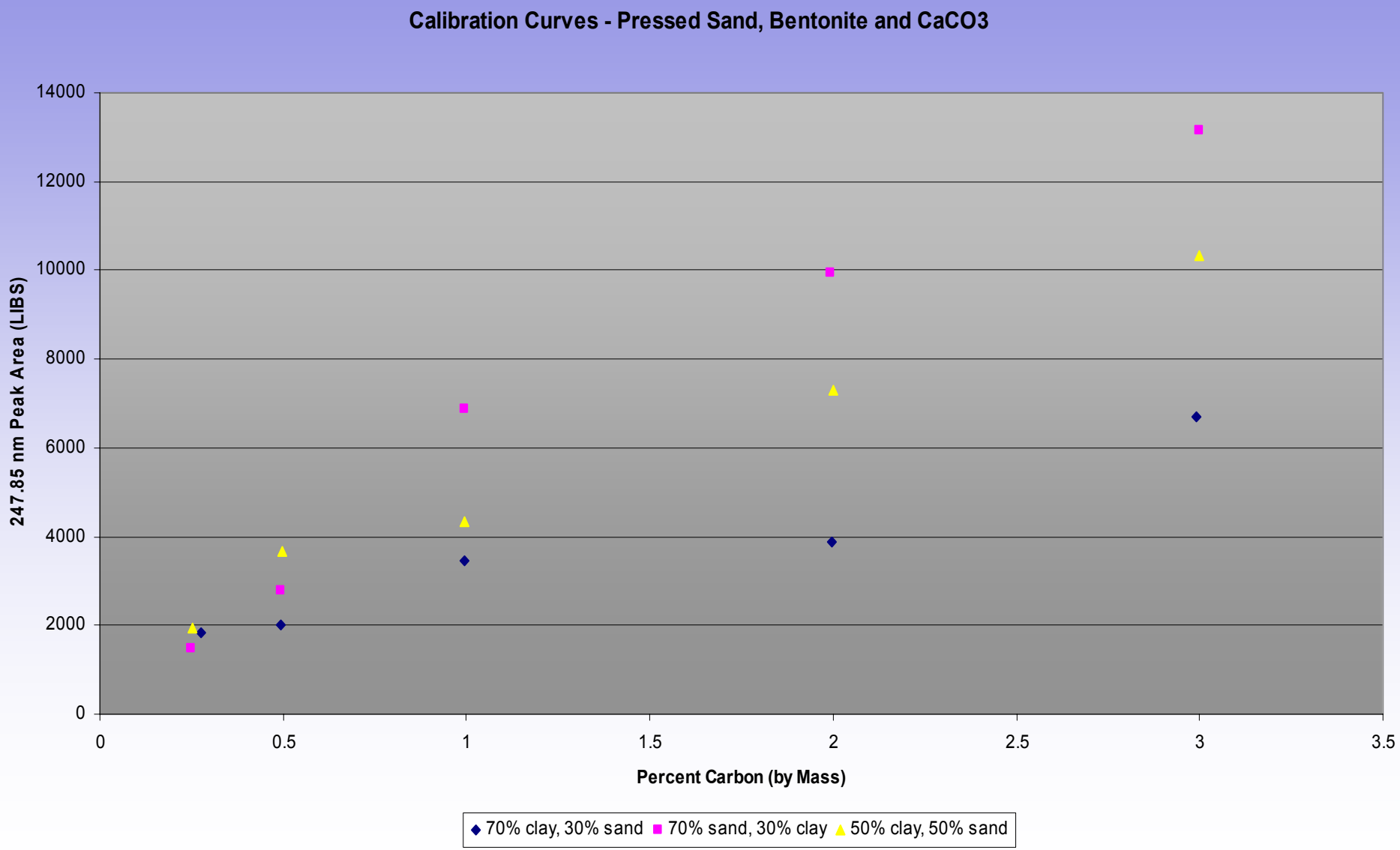
Calibration Curves for all Soils



Calibration for Different Soil Textures



Results from "Synthetic" Soils



The Big Challenge

- Goal: Determine total soil carbon using LIBS in the field
- Need to perform a calibration while in the field
- Appears that the LIBS signal is sensitive to soil texture
- Each field has a different response or sensitivity to the technique

Chemometric Techniques

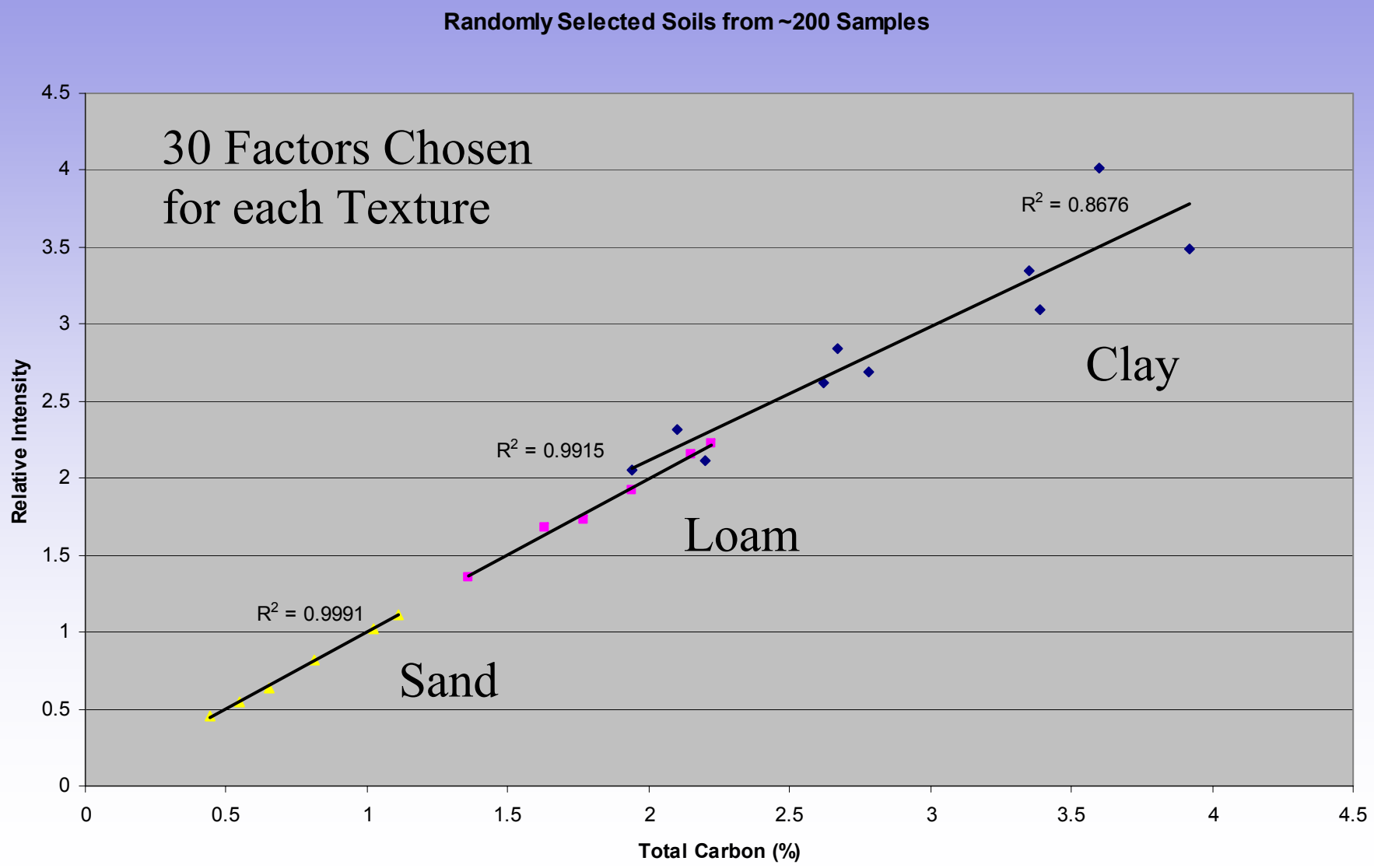
- Use other regions in the LIBS spectra to adjust or correct for the changes in sensitivity
- Algorithm looks for regions in the spectra that correlate either positively or negatively with the element of interest (carbon)
- Software goes through iterations, applying weights to regions of the spectra until the model fails to improve

PCR and PLS

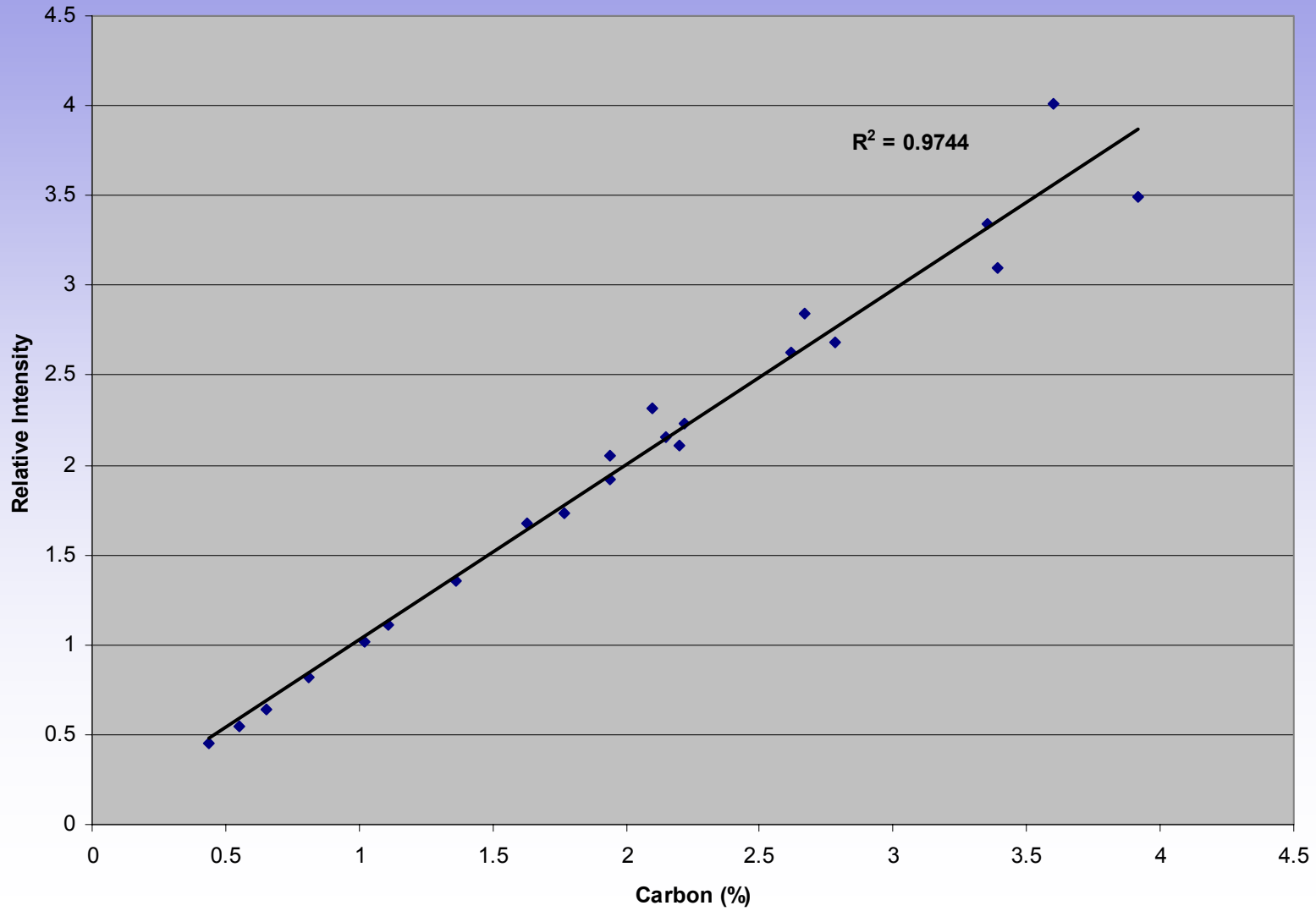
- Principal Components Regression – Factors are chosen that best characterize variations in the data and apply the best combination of these factors.

- Partial Least Squares – The first factor is chosen to give the best results for an element. Addition factors are chosen to improve on that result.

Applying PCR at LANL



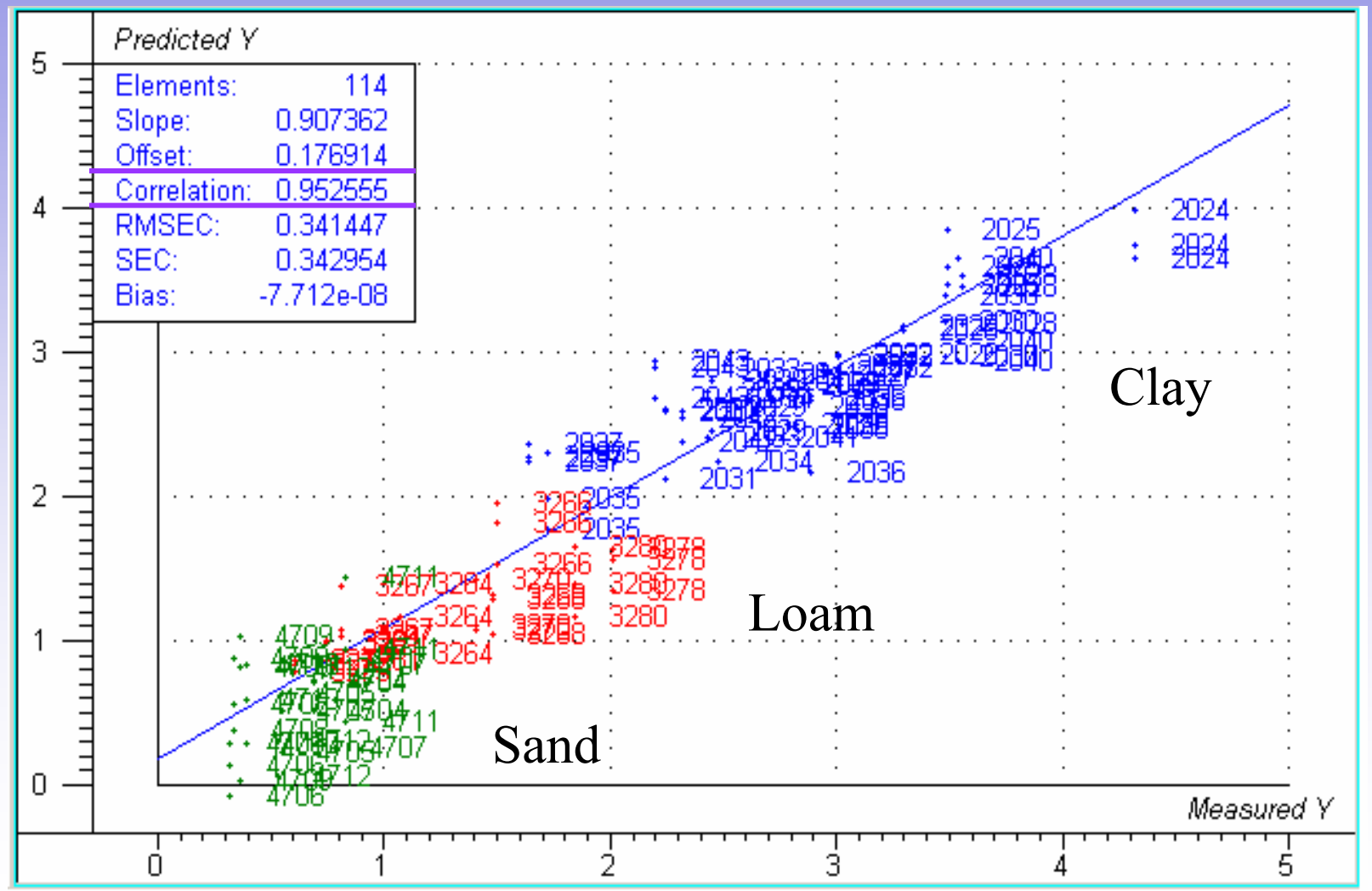
Calibration Curve for all Textures Using PCR



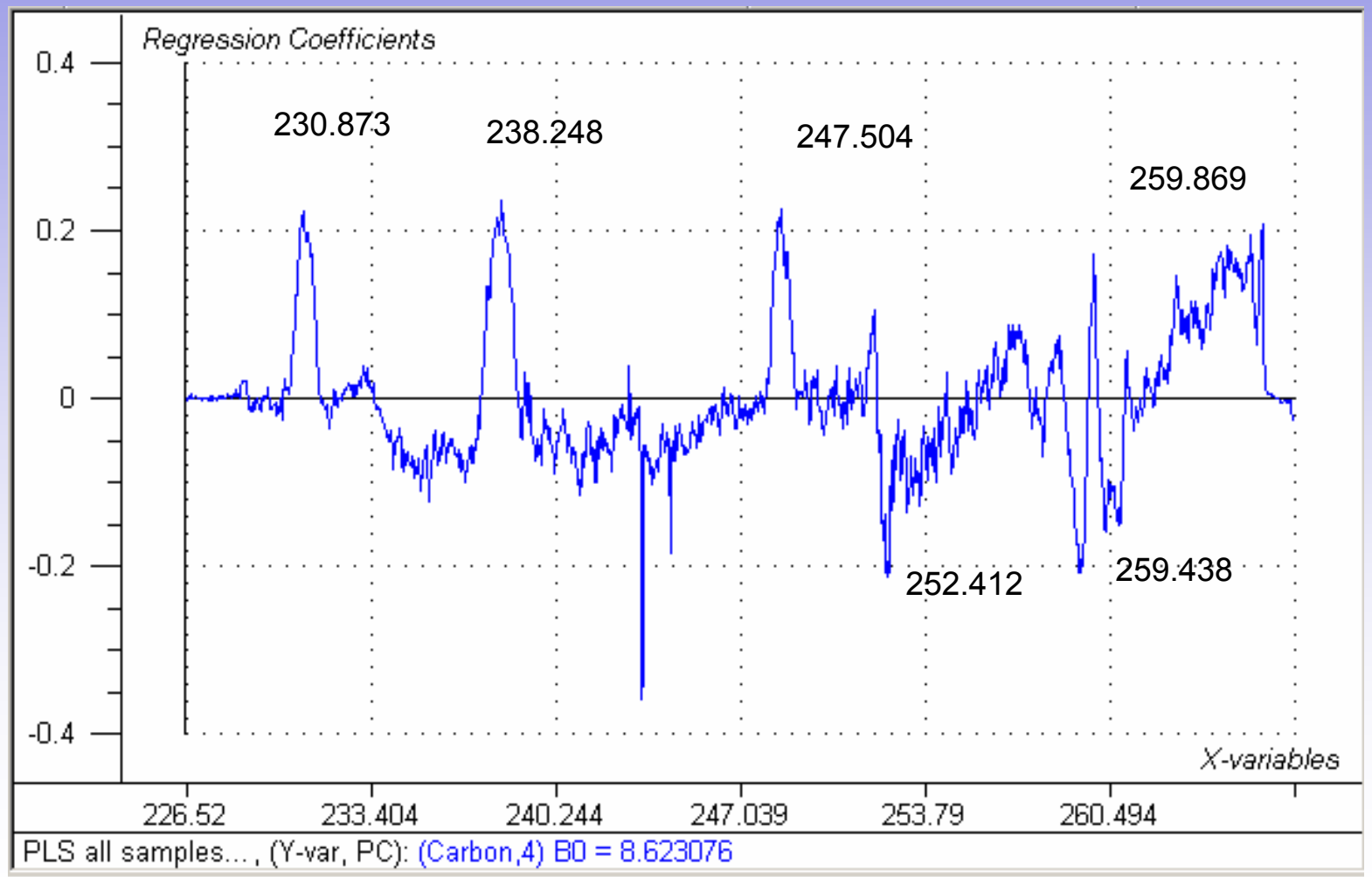
Applying Multivariate Analysis at ORNL

- 38 soils of the 3 textures were analyzed
- Soils were run in triplicate producing 114 spectra
- 2/3 of data used to construct a model
- 1/3 of data used to validate the model
- 532 nm excitation used at 45 and 90 mJ
- 1064 nm excitation to be completed in the near future

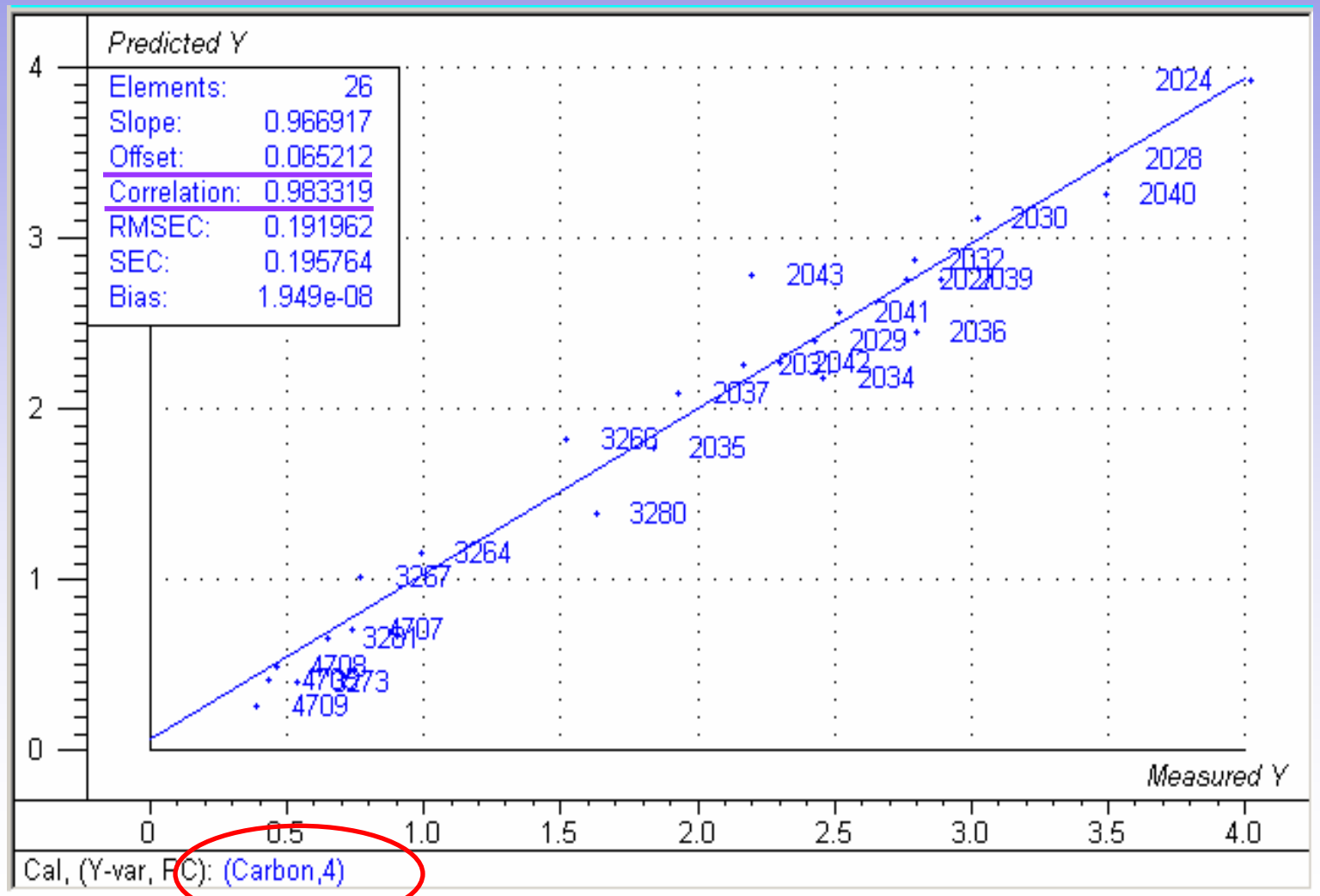
LIBS Data of 38 Soils in Triplicate using 532 nm Wavelength at 45 mJ Laser Power



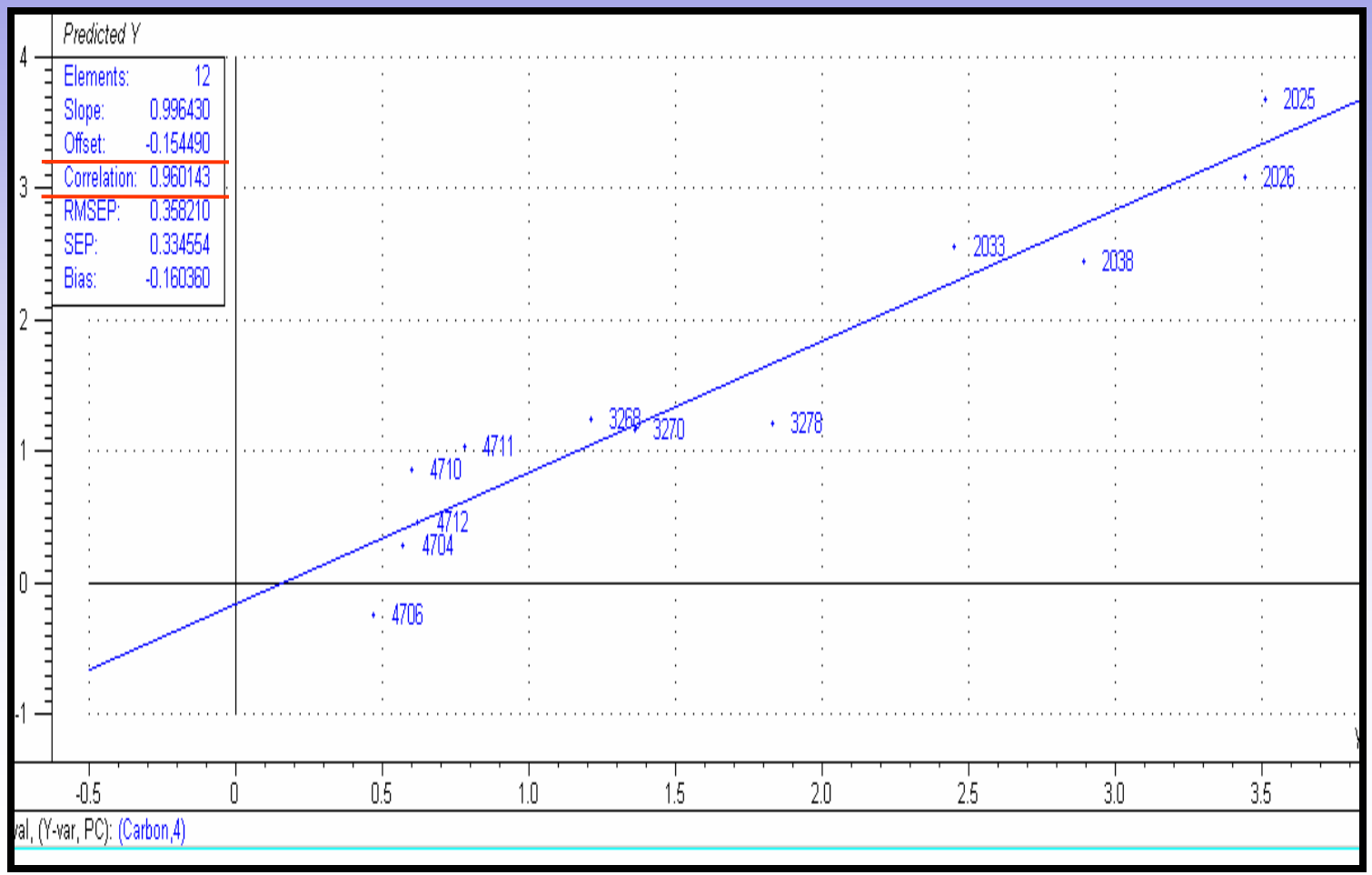
Significant Wavelengths to Build the 45 mJ Model for Prediction of Carbon Content



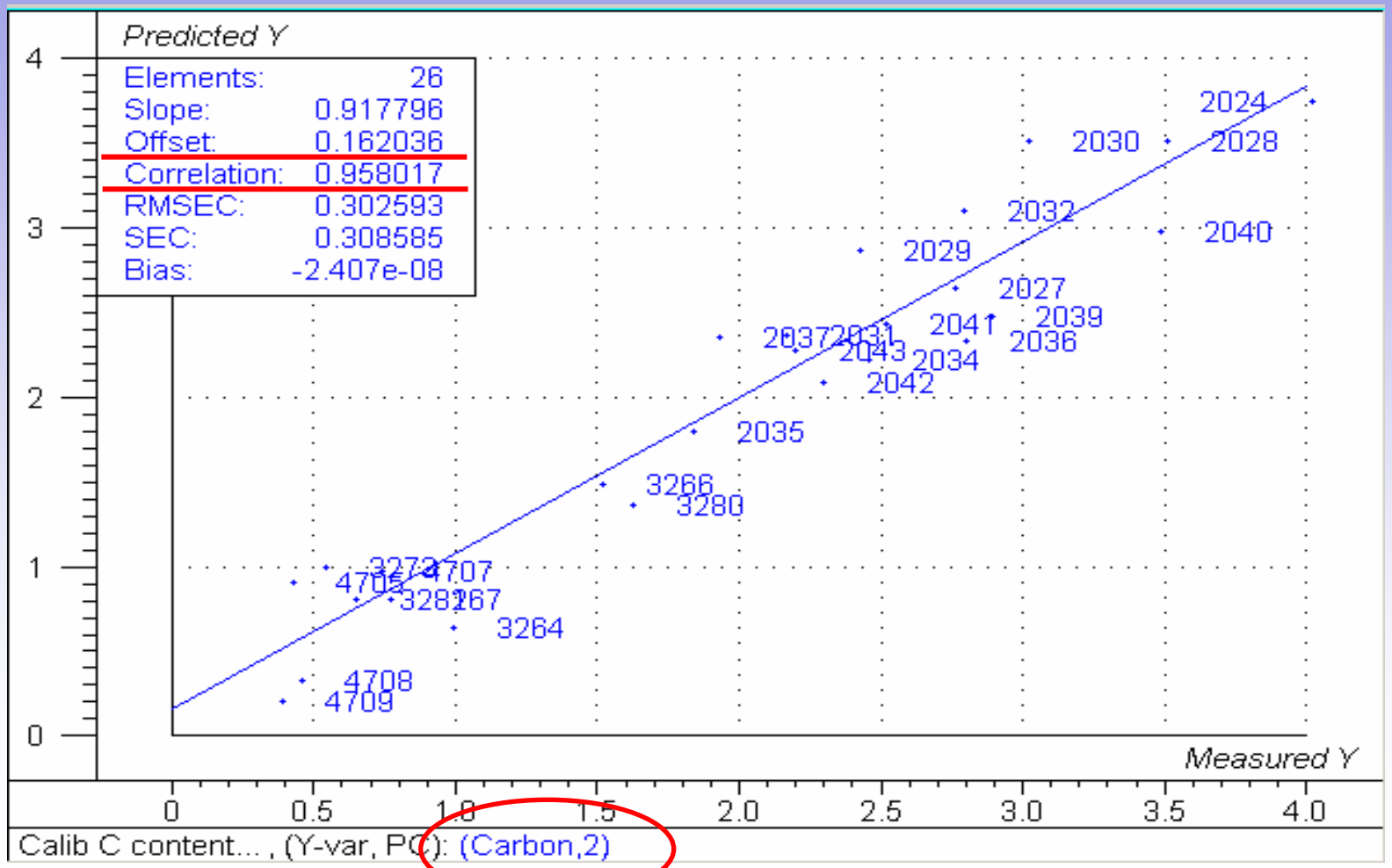
The 45 mJ Calibration Model is Built with 2/3 of the Data (26 samples)



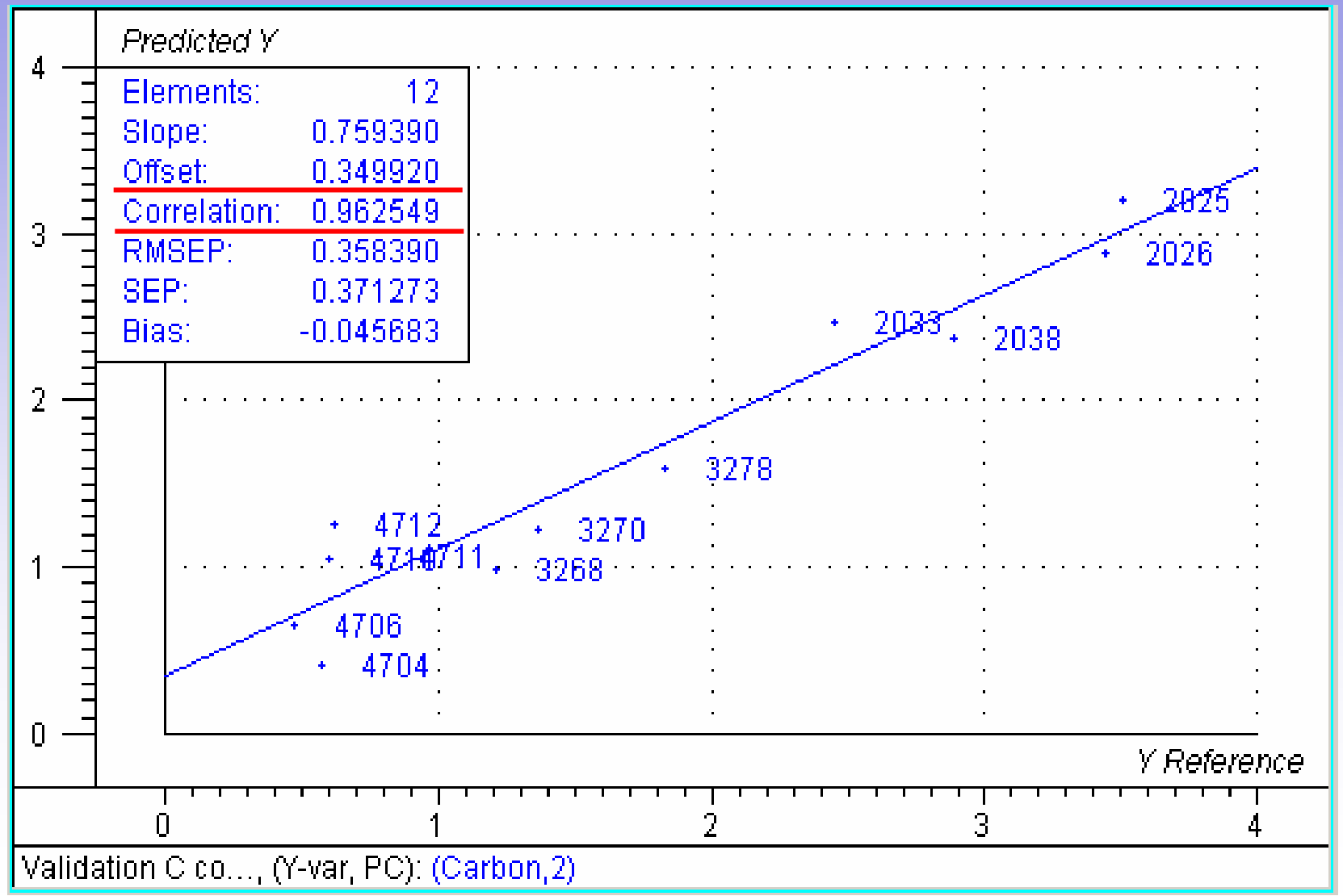
Validation of 45 mJ Model Using 12 Samples Not Included to Construct the Model



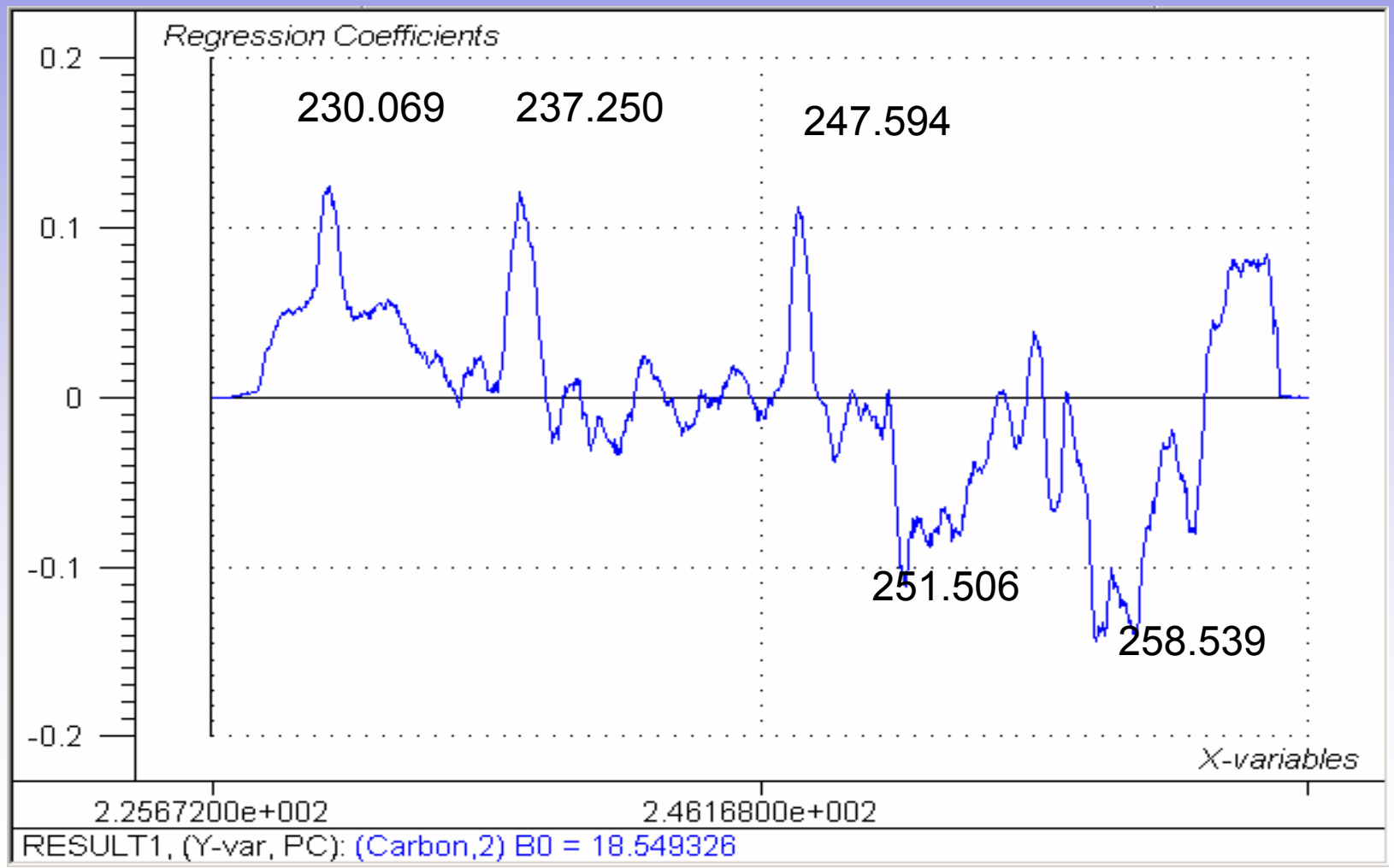
90mJ Calibration Model Using 2/3 of the Data



Validation of 90 mJ Model with 12 Samples Not Included to Construct the Model



Significant Wavelengths for Constructing 90 mJ Calibration Model



Conclusions

- ORNL: Multivariate analysis of LIBS data from all soil textures produced one calibration curve with a correlation of 0.98
- Validation of models at 45 and 90 mJ using samples not included to construct the models resulted in a correlation of 0.96
- The 45 mJ model required the use of 4 factors while the 90 mJ model required only 2 factors

Conclusions

- LANL: PCR analysis of LIBS data from randomly selected sands, loams and clays produced a calibration curve with a correlation of 0.97
- Different factors or components were used for each texture
- 30 factors were used

Thanks

- NETL for funding at LANL
- Research team at LANL, ORNL and UTenn
- Your Attention

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